

DESCRIPTION

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EXTERNAL PREPARATION FOR SKIN

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This is an application filed pursuant to 35 U.S.C. Section 111(a) with claiming the benefit of U.S. provisional application Serial No. 60/560,607 filed April 9, 2004 under the provision of 35 U.S.C. 111(b), pursuant to 35 U.S.C. Section 119(e)(1).

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TECHNICAL FIELD

The present invention relates to a novel external preparation for skin. Specifically, the present invention relates to an external preparation for skin comprising multi-branched polysaccharide derivatives, having an effect of maintaining the skin moisture and turgor.

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BACKGROUND ART

As a compound having an effect on maintaining the moisture of the skin in an external preparation for skin, a moisturizer is often used. A moisturizer is blended in an external preparation for skin for the purpose of preventing moisture from evaporating, controlling the moisture in the skin surface, and imparting a moist feeling as well as moisture. The moisture amount in the corneum layer of the skin closely relates to a protective function against a variety of stimuli from the surroundings, and plays an important role in anti-aging of the skin, or a feeling such as a moist feeling or a smooth feeling. This moisture retention in the corneum layer is generally controlled by NMF (natural moisturizing factor) and sebaceous membrane, however, its function is decreased easily due to aging or a stimulus from the surroundings. Therefore, to

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replenish a moisturizing component thereof is one of the important factors for an external preparation for skin, in particular a cosmetic product. Examples of the moisturizing component for replenishing moisture to the skin include, as the same biological component or an analogous component, an amino acid, peptide, protein, saccharide, polysaccharide, lipid, glycoprotein and the like.

For example, a cosmetic containing a dipeptide such as alanylglutamine blended therein (JP-A-08-325131), a cosmetic containing a saccharide such as plant-derived glycogen (JP-A-11-180818), and a cosmetic containing mucopolysaccharide blended therein with plant-derived glycogen (JP-A-2001-89381) are known. However, these cosmetics involve disadvantages that amino acid contained therein gives heavy feeling to the skin and does not easily fit in with the skin, and that a dipeptide, in form of a low molecular weight compound having a high solubility, may easily solve out from the external preparation having been applied onto the skin. In addition, a polysaccharide such as glycogen or mucopolysaccharide is not suitably employed as an ingredient for skin external preparations since its straight-chain structure rather causes uncomfortable taut feeling to the skin when the skin is dry, while such a polysaccharide is generally blended in external preparations as material having high moisture retention and skin compatibility. Moreover, a property for retaining skin moisture and turgor for a sufficient length of time against fluctuations in temperature and humidity and sweating cannot be achieved by cosmetics containing such a conventional ingredient. Further, there has been proposed an aqueous cosmetic using microorganism-derived polysaccharide (JP-A-2002-53426). However, polysaccharides derived from natural substances like those mentioned above consist of multiple types of monosaccharide with a variety of composing ratios and structures,

and therefore the diversity makes the quality control of the cosmetic difficult. Moreover, such a cosmetic involves a problem that aggregation often occurs to make the components uneven and generate gelation and/or precipitation, which causes uncomfortable feeling when applied onto the skin. As other moisture retaining agents, polyalcohols such as glycerin, propylene glycol and butylene glycol are used, and these compounds not only retain moisture but also have influences on feeling upon using the cosmetic.

Animal-derived compounds such as proteins such as collagen and keratin and hydrolysates thereof and placenta essence extracted from bovine placenta are also used as moisturizers in some cases, however, due to the decreased reliance on the safety, as more and more countries tend to prohibit uses of such animal-derived compounds in external preparations for skin, the industrial world is shifting toward compounds which have safer origins.

DISCLOSURE OF INVENTION

An object of the present invention is to provide an external preparation for skin which can give sufficient moisture and turgor to the skin. For the purpose of attaining the object, the present invention provides an external preparation for skin having high moisture retention property with little moisture eluting out therefrom so that the skin can keep sufficient moisture, giving no uncomfortable taut feeling upon using it even when the skin is in a dry state, being uniform in the structure and components and easy to control the quality, and having safe ingredients so that the external preparation can be used with ease from the viewpoint of safety. More specifically, an object of the invention is to provide an external preparation for skin containing a multi-branched polysaccharide and/or a derivative thereof which is a synthetic polymer derived from anhydrosaccharide.

As a result of intensive investigations to solve this problem, the present inventors have found out that by blending a multi-branched polysaccharide and/or a derivative thereof which consists of saccharides as constituting unit in an external preparation for skin, the external preparation for skin can have properties of giving sufficient moisture to the skin, and can be remarkably improved in adhesion to and affinity for the skin, providing a comfortable touch to the skin even in a dry condition, and thus completed the present invention.

Accordingly, the invention relates to the following items.

[1] An external preparation for skin, which comprises a multi-branched polysaccharide derivative with multi-branched polysaccharide skeleton consisting of saccharides as constituent units, wherein at least one of hydroxyl(OH) groups in the multi-branched polysaccharide skeleton is substituted by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon groups or a hydrocarbon having 1 to 30 carbon groups which has hetero atom).

[2] The external preparation for skin according to [1], wherein the multi-branched polysaccharide skeleton comprises a polymer consisting of monomers of anhydrosaccharide and/or anhydrosaccharide derivative in which at least one hydroxyl(OH) group is substituted by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon groups or a hydrocarbon having 1 to 30 carbon groups which has hetero atom).

[3] The external preparation for skin according to [2], wherein the anhydrosaccharide or the anhydrosaccharide moiety in the anhydrosaccharide derivative is at least one compound selected from the group consisting of 1,6-anhydrosaccharide, 1,4-anhydrosaccharide, 1,3-anhydrosaccharide, 1,2-anhydrosaccharide and 5,6-anhydrosaccharide.

[4] The external preparation for skin according to [2], wherein the polymer is obtained by cation polymerization or anion polymerization.

[5] The external preparation for skin according to [1], wherein the branching degree of the multi-branched polysaccharide is 0.05 to 1.00.

[6] The external preparation for skin according to any one of [1] to [5], wherein the amount of the multi-branched polysaccharide contained therein is 0.1 to 80 mass %.

[7] A cosmetic comprising the external preparation for skin according to any one of [1] to [6].

[EFFECTS OF THE INVENTION]

By using a multi-branched polysaccharide derivative, which consists of saccharides as constituting units, an external preparation for skin which gives sufficient moisture to the skin, with improved adhesion to and affinity for the skin, to thereby retain skin moisture and skin turgor and provide a comfortable touch of the skin even in a dry condition, can be obtained.

DETAILED DESCRIPTION OF THE INVENTION

Any multi-branched polysaccharide can be used to constitute the skeleton of the multi-branched polysaccharide derivative according to the present invention without particular limitation so long as the polysaccharide is a compound composed of one or more types of saccharides. The compound has a structure where one single saccharide molecule containing multiple hydroxyl groups has three or more moieties for bonding with adjacent molecules, and thereby the compound structure is formed into a tree like structure having many branching points. Generally, many of polysaccharides existing as natural products are straight-chain polysaccharides or polysaccharides having not so many branching

points, both types having a main chain. In the multi-branched polysaccharide, with so many branching points being present therein, there is no clearly distinguishable main chain.

Examples of the saccharide constituting the multi-branched polysaccharide of the present invention may include, for example, as a pentose, ribose and deoxyribose, as a hexose, glucose, fructose, galactose and the like.

As a production method of the multi-branched polysaccharide of the present invention, a conventionally known method can be applied. For example, as a production method by a chemical synthesis method, a production method of obtaining a multi-branched polysaccharide by polymerizing a derivative of a monosaccharide as a monomer can be exemplified. Examples thereof include, as disclosed in JP-A-2003-252904, a production method of obtaining a multi-branched polysaccharide by ionic polymerization using an anhydrosaccharide as a monomer.

In this case, examples of the anhydrosaccharide may include 1,6-anhydrosaccharide, 1,4-anhydrosaccharide, 1,3-anhydrosaccharide, 1,2-anhydrosaccharide, 5,6-anhydrosaccharide, etc., and a derivative thereof. Specific examples may include 1,6-anhydro- β -D-glucopyranose, 1,6-anhydro- β -D-mannopyranose, 1,6-anhydro- β -D-galactopyranose, 1,6-anhydro- β -D-allopyranose, 1,6-anhydro- β -D-altropyranose, 1,4-anhydro- β -D-ribose, 1,4-anhydro- α -D-xylopyranose, 1,4-anhydro- α -L-arabinopyranose, 1,4-anhydro- α -D-lyxopyranose, 1,3-anhydro- β -D-glucopyranose, 1,3-anhydro- β -D-mannopyranose, 1,2-anhydro- α -D-glucopyranose, 1,2-anhydro- β -D-mannopyranose, 5,6-anhydro- α -D-glucopyranose, etc., and a derivative thereof.

In addition, as the ionic polymerization, cation polymerization and anion polymerization can be exemplified. Further, there is a production method of obtaining a multi-branched

polysaccharide by using an animal, plant or microorganism, or by using a method of raising, cultivating or culturing it. In this case, a multi-branched polysaccharide with a desired branching degree can be directly used. However, as disclosed in JP-A-8-41104, for example, by a method for producing a multi-branched polysaccharide having an increased branching degree, a branched polysaccharide may become a multi-branched polysaccharide.

The multi-branched polysaccharide derivative of the present invention has a structure in which part and/or all of the hydroxyl groups in the multi-branched polysaccharide that constitutes the skeleton have been substituted by substituent(s). Examples include a compound in which at least one of the hydroxyl groups (OH) of the multi-branched polysaccharide has been substituted by OR (wherein R represents a hydrogen atom, a hydrocarbon having 1 to 30 carbon atoms, or a hydrocarbon having 1 to 30 carbon atoms which has hetero atom).

Examples of the R may include, for example, a methyl group, ethyl group, propyl group, isopropyl group, butyl group, 1-methylpropyl group, 2-methylpropyl group, pentyl group, 1-methylbutyl group, 2-methylbutyl group, 3-methylbutyl group, 1-ethylpropyl group, hexyl group, 1-methylpentyl group, 2-methylpentyl group, 3-methylpentyl group, 4-methylpentyl group, 1-ethylbutyl group, 2-ethylbutyl group, heptyl group, 1-methylhexyl group, 2-methylhexyl group, 3-methylhexyl group, 4-methylhexyl group, 5-methylhexyl group, 1-ethylpentyl group, 2-ethylpentyl group, 3-ethylpentyl group, octyl group, 1-methylheptyl group, 2-methylheptyl group, 3-methylheptyl group, 4-methylheptyl group, 5-methylheptyl group, 6-methylheptyl group, 1-ethylhexyl group, 2-ethylhexyl group, 3-ethylhexyl group, 4-ethylhexyl group, 1-propylpentyl group, 2-propylpentyl group,

nonyl group, decyl group, undecyl group, 10-undecenyl group, dodecyl group, tridecyl group, tetradecyl group, pentadecyl group, hexadecyl group, 9-hexadecenyl group, heptadecyl group, octadecyl group, isostearyl group, cis-9-octadecenyl group, 11-octadecenyl group, cis-cis-9,12-octadecadienyl group, 9,12,15-octadecatrienyl group, 6,9,12-octadecatrienyl group, 9,11,13-octadecatrienyl group, nonadecyl group, 2,6,10,14-tetramethyl pentadecyl group, icosanyl group, 8,11-icosadienyl group, 5,8,11-icosatrienyl group, 5,8,11,14-icosatetraenyl group, 3,7,11,15-tetramethylhexadecyl group, heneicosanyl group, docosanyl group, acetyl group, propionyl group, isopropionyl group, butyryl group, 1-methylpropionyl group, 2-methylpropionyl group, valeryl group, 1-methylbutyryl group, 2-methylbutyryl group, 3-methylbutyryl group, 1-ethylpropionyl group, hexanoyl group, 2-methylpentanoyl group, 3-methylpentanoyl group, 4-methylpentanoyl group, 2-ethylbutanoyl group, heptanoyl group, 2-methylhexanoyl group, 3-methylhexanoyl group, 4-methylhexanoyl group, 2-ethylpentanoyl group, 3-ethylpentanoyl group, octanoyl group, 2-methylheptanoyl group, 3-methylheptanoyl group, 4-methylheptanoyl group, 5-methylheptanoyl group, 6-methylheptanoyl group, 2-ethylhexanoyl group, 3-ethylhexanoyl group, 4-ethylhexanoyl group, 2-propylpentanoyl group, nonanoyl group, decanoyl group, undecanoyl group, 10-undecenoyl group, dodecanoyl group, tridecanoyl group, tetradecanoyl group, pentadecanoyl group, hexadecanoyl group, 9-hexadecenoyl group, heptadecanoyl group, octadecanoyl group, isostearyl group, cis-9-octadecenoyl group, 11-octadecenoyl group, cis,cis-9,12-octadecadienoyl group, 9,12,15-octadecatrienoyl group, 6,9,12-octadecatrienoyl group, 9,11,13-octadecatrienoyl group, nonadecanoyl group, 2,6,10,14-tetramethylpentadecanoyl group, icosanoyl group, 8,11-icosadienoyl group,

5,8,11-icosatrienoyl group, 5,8,11,14-icosatetraenoyl group, 3,7,11,15-tetramethylhexadecanoyl group, heneicosanoyl group, docosanoyl group, phosphatidyl group and the like. Further, a compound in which R has been bound with an isocyanate group and the like are also included.

As the synthetic method of the multi-branched polysaccharide derivative of the present invention, for example, a method of synthesizing a multi-branched polysaccharide derivative by modifying a hydroxyl group of a saccharide with a desired functional group after obtaining a multi-branched polysaccharide for constituting the skeleton, or a method of synthesizing a multi-branched polysaccharide derivative by polymerization after modifying a hydroxyl group of an anhydrosaccharide with a desired functional group to serve as a monomer of a multi-branched polysaccharide may be employed.

With regard to the modification of the hydroxyl group, for example, a method by a common esterification reaction using a carboxylic acid derivative can be employed. Specific examples include a method of performing reaction by using carboxylic acid as an acid chloride or a mixed acid anhydride, a method of performing reaction by using carbodiimide, a method of using an acid anhydride and the like. Further, in the case of a compound having an isocyanate group, a modification method of forming an urethane bond by heating or by using a catalyst such as a tin-based catalyst or an amine-based catalyst, and the like can be employed.

The branching degree of the multi-branched polysaccharide constituting the skeleton of the multi-branched polysaccharide derivative of the present invention is 0.05 to 1.00, preferably 0.2 to 1.0, more preferably 0.4 to 1.0. The multi-branching degree in this case is generally calculated with Frechet formula as shown below.

Branching Degree = (number of dendritic units + number of polymer ends) / (number of dendritic units + number of polymer ends + number of linear chain units)

5 Examples of the method of blending the multi-branched polysaccharide to be used in the present invention into an external preparation for skin include a method of producing an external preparation for skin by mixing it in as a solid, powder or semisolid, a method of producing an external preparation for skin by mixing
10 it in as an aqueous solution, a method of producing an external preparation for skin by mixing it in as a solution of an alcohol or an appropriate solvent, and a method of producing an external preparation for skin by mixing it in or adding by other known methods.

15 The multi-branched polysaccharide to be used in the present invention can be isolated as, for example, a form of powder, however, a solution obtained in the process of the production can be directly blended in an external preparation for skin.

 The multi-branched polysaccharide to be used in the present
20 invention, as long as the blending amount does not hinder formation of the external preparation for skin as cosmetics, can be blended in an amount of 0.01 to 100 % by mass, preferably from 0.1 to 80 % by mass, more preferably at 1 to 50 % by mass. If the blending amount is less than 0.01 % by mass based on the external preparation
25 for skin, adhesiveness and affinity to the skin are not sufficient, and a feeling such as a moisturizing feeling to the skin cannot be obtained sufficiently in some cases. It can be blended within such a range that essential functions of the external preparation for skin may not be impaired.

30 The term "external preparation for skin" used in the present invention includes cosmetics, detergents, bath agents, soaps and

the like which are used in direct contact with the skin.

Examples of the external preparation for skin of the present invention include in a wide sense, for example, skin milk, skin cream, foundation cream, massage cream, cleansing cream, shaving
5 cream, cleansing foam, skin lotion, lotion, facial mask, lip rouge, rouge, eye shadow, manicure, soap, body shampoo, hand soap, shampoo, hair conditioner, hair tonic, hair treatment, hair cream, hair spray, hair growth tonic, baldness remedy, hair dye, shmaltz, hair remover, anti-dandruff lotion, toothpaste, artificial teeth
10 adhesive, gargle, permanent wave agent, curling agent, styling agent, ointment, cataplasm, tape, bath agent, adiaphoretic, sun protectant and the like, and any type is included as long as it is used in contact with the skin. In particular, a preferred use of the external preparation for skin of the present invention is
15 a cosmetic product. In addition, the user may be anyone regardless of sex or age. Further, products to be used in contact with the skin of animals other than human are also included.

Examples of the form of the present invention include many forms such as powder, granule, tablet, gel and foam, as well as
20 solid, liquid, semisolid and gas.

In the external preparation for skin of the present invention, as a component other than the multi-branched polysaccharide and or derivative thereof, components generally used in an external preparation for skin can be blended within the range that does
25 not impair the effect of this invention, as needed. Examples of components include compounds blendable in cosmetic products, compounds serving as raw materials for quasi-drug products, drug products and medicinal additives.

Examples of such an ingredient include hydrocarbons such
30 as ozokerite, α -olefin oligomer, light isoparaffin, light liquid isoparaffin, squalene, squalane, synthetic squalane,

phytosqualane, ceresin, paraffin, polyethylene powder, polybutene, microcrystalline wax, liquid isoparaffin, liquid paraffin, mineral oil and vaseline;

natural waxes such as jojoba oil, carnauba wax, candelilla wax, rice bran wax, shellac, lanolin, mink sebaceous wax, spermaceti wax, sugarcane wax, sperm whale oil, beeswax and montan wax, natural fats and fatty oils such as avocado oil, almond oil, olive oil, extra virgin olive oil, sesame seed oil, rice bran oil, rice oil, rice germ oil, corn oil, safflower oil, soybean oil, maize oil, rape seed oil, persic oil, palm kernel oil, palm oil, castor oil, sunflower oil, high oleic sunflower oil, grape seed oil, cotton seed oil, coconut oil, hydrogenated coconut oil, beef tallow, hydrogenated oil, horse oil, mink oil, yolk oil, yolk fat oil, rose hip oil, kukui nut oil, evening primrose oil, wheat germ oil, peanut oil, Camellia japonica oil, Camellia kissi oil, cacao butter, Japan wax, beef bone tallow, nest's-foot oil, swine tallow, equine tallow, ovine tallow, shea butter, macadamia nut oil and meadowfoam seed oil;

fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid, γ -linolenic acid, isostearic acid, 12-hydroxystearic acid, undecylenic acid and coconut oil fatty acid;

higher alcohols such as isostearyl alcohol, octyl dodecanol, hexyl decanol, cholesterol, phytosterol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, behenyl alcohol and cetostearyl alcohol;

alkylglyceryl ethers such as batyl alcohol, chimyl alcohol, serachyl alcohol and isostearyl glyceryl ether;

esters such as isopropyl myristate, butyl myristate, isopropyl palmitate, ethyl stearate, butyl stearate, ethyl oleate,

ethyl linoleate, isopropyl linoleate, cetyl caprylate, hexyl
laurate, isooctyl myristate, decyl myristate, myristyl myristate,
cetyl myristate, octadecyl myristate, cetyl palmitate, stearyl
stearate, decyl oleate, oleyl oleate, cetyl ricinoleate, isostearyl
5 laurate, isotridecyl myristate, isocetyl myristate, isostearyl
myristate, octyldodecyl myristate, 2-ethylhexyl palmitate,
isocetyl palmitate, isostearyl palmitate, 2-ethylhexyl stearate,
isocetyl stearate, isodecyl oleate, octyldodecyl oleate,
octyldodecyl ricinoleate, ethyl isostearate, isopropyl
10 isostearate, cetyl 2-ethylhexanoate, cetostearyl
2-ethylhexanoate, stearyl 2-ethylhexanoate, hexyl isostearate,
ethylene glycol dioctanoate, ethylene glycol dioleate, propylene
glycol dicaprylate, propylene glycol dicaprylate/dicaprate,
propylene glycol dicaprate, propylene glycol dioleate, neopentyl
15 glycol dicaprate, neopentyl glycol dioctanoate, glyceryl
tricaprylate, glyceryl tri 2-ethyl hexanoate, glyceryl
tricaprylate/tricaprate, glyceryl
tricaprylate/tricaprate/tristearate, glyceryl triundecylate,
glyceryl triisopalmitate, glyceryl triisostearate,
20 trimethylolpropane tri 2-ethylhexanoate, trimethylolpropane
triisostearate, pentaerythrityl tetra 2-ethylhexanoate,
pentaerythrityl tetramyristate, pentaerythrityl tetraisostearate,
diglyceryl tetraisostearate, octyldodecyl neopentanoate,
isocetyl octanoate, isostearyl octanoate, 2-ethylhexyl
25 isopelargonate, hexyldecyl dimethyloctanoate, octyldodecyl
dimethyloctanoate, 2-ethylhexyl isopalmitate, isocetyl
isostearate, isostearyl isostearate, octyldodecyl isostearate,
lauryl lactate, myristyl lactate, cetyl lactate, octyldodecyl
lactate, triethyl citrate, acetyltriethyl citrate, acetyltributyl
30 citrate, trioctyl citrate, triisocetyl citrate, trioctyldodecyl
citrate, diisostearyl malate, 2-ethylhexyl hydroxystearate, di

2-ethylhexyl succinate, diisopropyl adipate, diisobutyl adipate, dioctyl adipate, diheptylundecyl adipate, sebacate diethyl, diisopropyl sebacate, dioctyl sebacate, cholesteryl stearate, cholesteryl isostearate, cholesteryl hydroxystearate, 5 cholesteryl oleate, dihydrocholesteryl oleate, phytosteryl isostearate, phytosteryl oleate, isocetyl 12-stearoyl hydroxystearate, stearyl 12-stearoyl hydroxystearate, isostearyl 12-stearoyl hydroxystearate, polyoxyethylene (3) polyoxypropylene (1) cetyl ether acetate, polyoxyethylene (3) 10 polyoxypropylene (1) isocetyl ether acetate, isononyl isononanoate, octyl isononanoate, tridecyl isononanoate and isotridecyl isononanoate;

silicone oils such as methyl polysiloxane, methylphenyl polysiloxane, methyl hydrogen polysiloxane, methyl 15 cyclopolysiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, dodecamethyl cyclohexasiloxane, octamethyl trisiloxane, decamethyl tetrasiloxane, tetradecamethyl hexasiloxane, highly polymerized methyl polysiloxane, dimethylsiloxane-methyl (polyoxyethylene) siloxane-methyl (polyoxypropylene) siloxane copolymer, 20 dimethylsiloxane-methyl (polyoxyethylene) siloxane copolymer, dimethylsiloxane-methyl (polyoxypropylene) siloxane copolymer, dimethylsiloxane-methylcetyl oxysiloxane copolymer, dimethylsiloxane-methyl stearoxysiloxane copolymer, polyether 25 modified silicone, alcohol modified silicone, alkyl modified silicone and amino modified silicone;

polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, pentanediol, glycerin, 30 diglycerin, polyglycerin, isoprene glycol, 1,3-butylene glycol, 3-methyl-1,3-butanediol, 1,3-butanediol, 1,2-pentanediol and

1,2-hexanediol;

saccharides such as mannitol, sorbitol, xylitol, maltitol, erythritol, pentaerythritol, glucose, sucrose, fructose, lactose, maltose, xylose and trehalose;

5 polymers such as sodium alginate, carrageen, agar, furcellaran, guar gum, quince seed, Amorphophalus konjak (arum root) mannan, tamarind gum, tara gum, dextrin, starch, locust bean gum, gum arabic, gum gatti, karaya gum, gum tragacanth, arabinogalactan, pectin, quince, chitosan, curdlan, xanthan gum,
10 gellan gum, cyclodextrin, dextran, pullulan, microcrystalline cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, carboxy starch, cationized cellulose, starch phosphate ester, cationized guar gum,
15 carboxymethyl-hydroxypropylated guar gum, hydroxypropylated guar gum, albumin, casein, gelatin, sodium polyacrylate, polyacrylic amide, carboxyvinyl polymer, polyethylene imine, highly polymerized polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl ether, polyacryl amide, acrylic acid
20 copolymer, methacrylic acid copolymer, maleic acid copolymer, vinylpyridine copolymer, ethylene/acrylic acid copolymer, vinyl pyrrolidone based polymer, vinyl alcohol/vinyl pyrrolidone copolymer, nitrogen-substituted acrylamide based polymer, amino modified silicone, cationized polymer, dimethylacryl ammonium
25 based polymer, acrylic acid based anion polymer, methacrylic acid based anion polymer, modified silicone, acrylate/methacrylate alkyl (C 10 to 30) copolymer and polyoxyethylene/polyoxypropylene copolymer;

alcohols such as ethanol, isopropyl alcohol, 1-butanol,
30 2-butanol and benzyl alcohol;

anionic surfactants such as coconut oil fatty acid potassium,

coconut oil fatty acid sodium, coconut oil fatty acid
triethanolamine, potassium laurate, sodium laurate,
triethanolamine laurate, potassium myristate, sodium myristate,
isopropanolamine myristate, potassium palmitate, sodium palmitate,
5 isopropanolamine palmitate, potassium stearate, sodium stearate,
triethanolamine stearate, potassium oleate, sodium oleate, castor
oil fatty acid sodium, zinc undecylate, zinc laurate, zinc myristate,
magnesium myristate, zinc palmitate, zinc stearate, calcium
stearate, magnesium stearate, aluminum stearate, calcium myristate,
10 magnesium myristate, aluminum dimyristate, aluminum isostearate,
polyoxyethylene lauryl ether acetate, sodium polyoxyethylene
lauryl ether acetate, polyoxyethylene tridecyl ether acetate,
sodium polyoxyethylene tridecyl ether acetate, sodium stearyl
lactate, sodium isostearyl lactate, sodium lauroyl sarcosine,
15 coconut oil fatty acid sarcosine, sodium coconut oil fatty acid
sarcosine, coconut oil fatty acid sarcosine triethanolamine,
lauroyl sarcosine, potassium lauroyl sarcosine, lauroyl sarcosine
triethanolamine, oleoyl sarcosine, sodium myristoyl sarcosine,
sodium stearyl glutamate, coconut oil fatty acid acyl glutamic
20 acid, potassium coconut oil fatty acid acyl glutamate, sodium
coconut oil fatty acid acyl glutamate, coconut oil fatty acid acyl
glutamate triethanolamine, lauroyl acyl glutamic acid, potassium
lauroyl acyl glutamate, sodium lauroyl acyl glutamate, lauroyl acyl
glutamate triethanolamine, myristoyl acyl glutamic acid, potassium
25 myristoyl acyl glutamate, sodium myristoyl acyl glutamate,
stearyl acyl glutamic acid, potassium stearyl acyl glutamate,
disodium stearyl acyl glutamate, sodium hydrogenated beef tallow
fatty acid acyl glutamate, sodium coconut oil fatty
acid/hydrogenated beef tallow fatty acid acyl glutamate, sodium
30 coconut oil fatty acid methylalanine, lauroyl methylalanine, sodium
lauroyl methylalanine, lauroyl methylalanine triethanolamine,

sodium myristoyl methylalanine, sodium lauroyl methyltaurine, potassium coconut oil fatty acid methyltaurine, sodium coconut oil fatty acid methyltaurine, magnesium coconut oil fatty acid methyltaurine, sodium myristoyl methyltaurine, sodium palmitoyl methyltaurine, sodium stearoyl methyltaurine, sodium oleoyl methyltaurine, sodium alkane sulfonate, sodium tetradecene sulfonate, sodium sulfosuccinate dioctyl, disodium lauryl sulfosuccinate, sodium coconut oil fatty acid ethyl ester sulfonate, sodium lauryl sulfate, triethanolamine lauryl sulfate, sodium cetyl sulfate, triethanolamine alkyl (11,13,15) sulfate, sodium alkyl (12,13) sulfate, triethanolamine alkyl (12,13) sulfate, alkyl (12,14,16) ammonium sulfate, diethanolamine alkyl (12 to 13) sulfate, triethanolamine alkyl (12 to 14) sulfate, triethanolamine alkyl (12 to 15) sulfate, magnesium coconut oil alkyl sulfate/triethanolamine, lauryl ammonium sulfate, potassium lauryl sulfate, magnesium lauryl sulfate, monoethanolamine lauryl sulfate, diethanolamine lauryl sulfate, sodium myristyl sulfate, sodium stearyl sulfate, sodium oleyl sulfate, triethanolamine oleyl sulfate, sodium polyoxyethylene lauryl ether sulfate, triethanolamine polyoxyethylene lauryl ether sulfate, sodium polyoxyethylene (1) alkyl (11,13,15) ether sulfate, triethanolamine polyoxyethylene (1) alkyl (11,13,15) ether sulfate, sodium polyoxyethylene (3) alkyl (11 to 15) ether sulfate, sodium polyoxyethylene (2) alkyl (12,13) ether sulfate, sodium polyoxyethylene (3) alkyl (12 to 14) ether sulfate, sodium polyoxyethylene (3) alkyl (12 to 15) ether sulfate, sodium polyoxyethylene (2) lauryl ether sulfate, sodium polyoxyethylene (3) myristyl ether sulfate, sodium higher fatty acid alkanol amide sulfate ester, lauryl phosphate, sodium lauryl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, polyoxyethylene oleyl ether phosphate, polyoxyethylene lauryl ether phosphate,

sodium polyoxyethylene lauryl ether phosphate, polyoxyethylene
cetyl ether phosphate, sodium polyoxyethylene cetyl ether phosphate,
polyoxyethylene stearyl ether phosphate, polyoxyethylene oleyl
ether phosphate, sodium polyoxyethylene oleyl ether phosphate,
5 polyoxyethylene alkylphenyl ether phosphate, sodium
polyoxyethylene alkylphenyl ether phosphate, triethanolamine
polyoxyethylene alkylphenyl ether phosphate, polyoxyethylene
octyl ether phosphate, polyoxyethylene (10) alkyl (12,13) ether
phosphate, polyoxyethylene alkyl (12 to 15) ether phosphate,
10 polyoxyethylene alkyl (12 to 16) ether phosphate, triethanolamine
polyoxyethylene lauryl ether phosphate and diethanolamine
polyoxyethylene oleyl ether phosphate;
cationic surfactants such as dioctylamine,
dimethylstearylamine, trilaurylamine, diethylaminoethylamide
15 stearate, lauryl trimethylammonium chloride, cetyl
trimethylammonium chloride, cetyl trimethylammonium bromide,
cetyl trimethylammonium saccharin, stearyl trimethylammonium
chloride, alkyl (20 to 22) trimethylammonium chloride, lauryl
trimethylammonium bromide, alkyl (16,18) trimethylammonium
20 chloride, stearyl trimethylammonium bromide, stearyl
trimethylammonium saccharin, alkyl (28) trimethylammonium
chloride, di(polyoxyethylene) oleyl methylammonium (2EO) chloride,
dipolyoxyethylene stearyl methylammonium chloride,
polyoxyethylene (1) polyoxypropylene (25) diethylmethylammonium
25 chloride, tri(polyoxyethylene) stearyl ammonium (5EO) chloride,
distearyl dimethylammonium chloride, dialkyl (12 to 15)
dimethylammonium chloride, dialkyl (12 to 18) dimethylammonium
chloride, dialkyl (14 to 18) dimethylammonium chloride, dicocoyl
dimethylammonium chloride, dicetyl dimethylammonium chloride,
30 isostearyl lauryl dimethylammonium chloride, benzalkonium
chloride, myristyl dimethylbenzyl ammonium chloride, lauryl

dimethyl(ethylbenzyl) ammonium chloride, stearyl dimethylbenzyl ammonium chloride, lauryl pyridinium chloride, cetyl pyridinium chloride, lauroyl cholamino formylmethyl pyridinium chloride, stearyl cholamino formylmethyl pyridinium chloride, alkyl
5 isoquinolinium bromide, methyl benzethonium chloride and benzethonium chloride;

ampholytic surfactants such as

2-alkyl-N-carboxymethyl-N-hydroxyethyl imidazolium betaine,
alkyldiamino ethyl glycine hydrochloride, sodium lauryldiamino
10 ethyl glycine, sodium undecyl hydroxyethyl imidazolium betaine,
undecyl-N-carboxymethyl imidazolium betaine, disodium coconut oil
fatty acid acyl-N-carboxyethyl-N-hydroxyethyl ethylenediamine,
disodium coconut oil fatty acid
acyl-N-carboxyethoxyethyl-N-carboxyethyl ethylenediamine,
15 disodium coconut oil fatty acid
acyl-N-carboxymethoxyethyl-N-carboxymethyl ethylenediamine,
sodium laurylamino propionate, sodium laurylamino dipropionate,
triethanolamine laurylamino propionate, sodium palm oil fatty acid
acyl-N-carboxyethyl-N-hydroxyethyl ethylenediamine, betaine
20 lauryldimethylamino acetate, betaine coconut oil
alkyldimethylamino acetate, betaine stearyl dimethylamino acetate,
sodium stearyldimethyl betaine, coconut oil fatty acid amidopropyl
betaine, palm oil fatty acid amidopropyl betaine, amidopropyl
acetate betaine laurate, amidopropyl betaine ricinoleate, stearyl
25 dihydroxyethyl betaine and lauryl hydroxysulfobetaine;

nonionic surfactants such as polyoxyethylene (10) alkyl
(12,13) ether, polyoxyethylene lauryl ether, polyoxyethylene cetyl
ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether,
polyoxyethylene (3,7,12) alkyl (12 to 14) ether, polyoxyethylene
30 tridecyl ether, polyoxyethylene myristyl ether,
polyoxyethylene-sec-alkyl (14) ether, polyoxyethylene isocetyl

ether, polyoxyethylene cetostearyl ether, polyoxyethylene (2,10,20) isostearyl ether, polyoxyethylene oleylcetyl ether, polyoxyethylene (20) arachyl ether, polyoxyethylene octyldodecyl ether, polyoxyethylene behenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene dinonylphenyl ether, polyoxyethylene (1) polyoxypropylene (1,2,4,8) cetyl ether, polyoxyethylene (5) polyoxypropylene (1,2,4,8) cetyl ether, polyoxyethylene (10) polyoxypropylene (1,2,4,8) cetyl ether, polyoxyethylene (20) polyoxypropylene (1,2,4,8) cetyl ether, polyoxyethylene polyoxypropylene lauryl ether, polyoxyethylene (3) polyoxypropylene (34) stearyl ether, polyoxyethylene (4) polyoxypropylene (30) stearyl ether, polyoxyethylene (34) polyoxypropylene (23) stearyl ether, polyoxyethylene polyoxypropylene cetyl ether, polyoxyethylene polyoxypropylene decyltetradecyl ether, polyethylene glycol monolaurate, ethylene glycol monostearate, polyethylene glycol monostearate, polyethylene glycol monooleate, ethylene glycol fatty acid ester, self-emulsifying ethylene glycol monostearate, diethylene glycol laurate, polyethylene glycol myristate, polyethylene glycol palmitate, diethylene glycol stearate, self-emulsifying polyethylene glycol (2) monostearate, polyethylene glycol isostearate, ethylene glycol dioctanoate, diethylene glycol dilaurate, polyethylene glycol dilaurate, polyethylene glycol (150) dipalmitate, ethylene glycol distearate, diethylene glycol distearate, polyethylene glycol distearate, ethylene glycol dioleate, polyethylene glycol dioleate, polyethylene glycol diricinoleate, polyoxyethylene (20) sorbitan monolaurate, polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (6) sorbitan monostearate, polyoxyethylene (20) sorbitan monostearate, polyoxyethylene (20) sorbitan tristearate, polyoxyethylene (6) sorbitan monooleate, polyoxyethylene (20)

sorbitan monooleate, polyoxyethylene (20) sorbitan trioleate, polyoxyethylene (20) coconut oil fatty acid sorbitan, polyoxyethylene (10 to 80) sorbitan monolaurate, polyoxyethylene sorbitan tristearate, polyoxyethylene (20) sorbitan isostearate, 5 polyoxyethylene (150) sorbitan tristearate, polyoxyethylene castor oil, polyoxyethylene hydrogenated castor oil, polyoxyethylene (10) hydrogenated castor oil, polyoxyethylene (20) hydrogenated castor oil, polyoxyethylene (40) hydrogenated castor oil, polyoxyethylene (50) hydrogenated castor oil, polyoxyethylene 10 (60) hydrogenated castor oil, lipophilic glycerin monostearate, lipophilic glycerin monooleate, self-emulsifying glycerin monostearate, coconut oil fatty acid glyceryl, glycerin laurate, glyceryl myristate, glyceryl isostearate, glyceryl ricinoleate, glyceryl monohydroxystearate, glycerinoleate, glyceryl linoleate, 15 glyceryl erucate, glyceryl behenate, wheat germ oil fatty acid glyceride, safflower oil fatty acid glyceryl, hydrogenated soybean fatty acid glyceryl, saturated fatty acid glyceride, cotton seed oil fatty acid glyceryl, monomyristate glyceryl monoisostearate, monotallowate glyceride, monolanolin fatty acid glyceryl, glyceryl 20 sesquioleate, glyceryl distearate, glyceryl diisostearate, glyceryl diarachidate, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitan monooleate, sorbitan sesquistearate, sorbitan sesquioleate, sorbitan tristearate, sorbitan trioleate, coconut 25 oil fatty acid sorbitan, sorbitan isostearate, sorbitan sesquiisostearate, sorbitan distearate, diglyceryl isopalmitate, poly(4 to 10) glyceryl monolaurate, poly(10) glyceryl monomyristate, poly(2 to 10) glyceryl monostearate, poly(2 to 10) glyceryl monoisostearate, poly(2 to 10) glyceryl monooleate, diglyceryl 30 sesquioleate, poly(2 to 10) glyceryl diisostearate, poly(6 to 10) glyceryl distearate, diglyceryl triisostearate,

poly(10)glyceryl tristearate, poly(10)glyceryl trioleate,
poly(2)glyceryl tetraisostearate, decaglyceryl pentastearate,
poly(6 to 10)glyceryl pentaoleate, poly(10)glyceryl heptastearate,
decaglyceryl decastearate, poly(10)glyceryl decaoleate,
5 concentrated poly(6)glyceryl ricinoleate, sucrose fatty acid ester,
coconut oil fatty acid sucrose ester, alkyl glucoside, coconut
oil alkyl dimethylamine oxide, lauryl dimethylamine oxide,
dihydroxyethyl lauryl dimethylamine oxide, stearyl dimethylamine
oxide, oleyl dimethylamine oxide and polyoxyethylene coconut oil
10 alkyl dimethylamine oxide;

natural surfactants such as saponin, lecithin, soybean
phospholipid, hydrogenated soybean phospholipid, soybean
lysophospholipid, hydrogenated soybean lysophospholipid, yolk
lecithin, hydrogenated yolk lysophosphatidylcholine,
15 phosphatidylcholine, phosphatidylethanolamine,
phosphatidylserine, sphingophospholipid, sphingomyelin,
ganglioside, bile acid, cholic acid, deoxycholic acid, sodium
cholate, sodium deoxycholate, spiculisporic acid, rhamnolipid,
trehalose lipid, sophorolipid and mannosyl erythritol lipid;

20 ultraviolet ray absorbers such as: para-aminobenzoic acid
derivatives such as para-aminobenzoic acid, ethyl
para-aminobenzoate, glyceryl para-aminobenzoate, amyl
para-dimethyl aminobenzoate and 2-ethylhexyl para-dimethyl
aminobenzoate; cinnamic acid derivatives such as benzyl cinnamate,
25 mono-2-ethyl hexanoate glyceryl dipara-methoxycinnamate, methyl
2,4-diisopropyl cinnamate, ethyl 2,4-diisopropyl cinnamate,
potassium para-methoxycinnamate, sodium para-methoxycinnamate,
isopropyl para-methoxycinnamate, 2-ethylhexyl
para-methoxycinnamate, 2-ethoxyethyl para-methoxycinnamate and
30 ethyl para-ethoxycinnamate; urocanic acid derivatives such as
urocanic acid and ethyl urocanate; benzophenone derivatives such

as 2,4-dihydroxybenzophenone,
2,2',4,4'-tetrahydroxybenzophenone, sodium
2-hydroxy-4-methoxy-5-sulfobenzophenone,
2-hydroxy-4-methoxybenzophenone-5-sulfonate,

5 2-hydroxy-4-methoxybenzophenone,
2,2'-dihydroxy-4,4'-dimethoxybenzophenone and sodium
2,2'-dihydroxy-4,4'-dimethoxy-5-sulfobenzophenone; salicylic
acid derivatives such as ethylene glycol salicylate,
salicylate-2-ethylhexyl, phenyl salicylate, benzyl salicylate,
10 p-tert-butylphenyl salicylate, homomenthyl salicylate and
salicylate-3,3,5-trimethylcyclohexyl;
2-(2'-hydroxy-5'-methoxyphenyl)benzotriazole and
4-tert-butyl-4'-methoxybenzoyl methane;

powders and color materials such as: kaolin, silicic
15 anhydride, magnesium aluminum silicate, sericite, talc, boron
nitride, mica, montmorillonite, hemp cellulose powder, wheat starch,
silk powder, maize starch; natural dyes such as nitro dyes, azo
dyes, nitrosodyes, triphenylmethane dyes, xanthene dyes, quinoline
dyes, anthraquinone dyes, indigo dyes, pyrene dyes, phthalocyanine
20 dyes, flavonoid, quinone, porphyrin, water soluble annatto, sepia
powder, caramel, guaiazulene, gardenia blue, gardenia yellow,
cochineal, shikonin, sodium copper chlorophyllin, paprika dye,
safflower red, safflower yellow, laccaic acid and riboflavin
butyrate ester; carbon black, yellow iron oxide, black iron oxide,
25 red iron oxide, iron blue, ultramarine blue, zinc oxide, chromium
oxide, titanium oxide, black titanium oxide, zirconium oxide,
chromium hydroxide, alumina, magnesium oxide, barium sulfate,
aluminum hydroxide, calcium carbonate, lithium cobalt titanate,
manganese violet and pearl pigment.

30 plant extracts such as Angelica keiskei extract, Uncaria
gambir extract, avocado extract, sweet hydrangea leaf extract,

Gynostemma pentaphyllum makino extract, Althaea officinalis extract, Arnica montana extract, oil soluble Arnica montana extract, almond extract, aloe extract, Japanese styrax benzoin extract, Ginkgo biloba extract, Stinging nettle extract, Orris rhizome root
5 extract, fennel extract, turmeric extract, dog rose fruit extract, Echinacea leaf extract, Scutellaria root extract, Phellodendron bark extract, Japanese captis extract, barley extract, okura extract, Hypericum perforatum extract, oil soluble Hypericum perforatum extract, Lamium album extract, oil soluble Lamium album
10 extract, Ononis spinosa root extract, Nasturtium officinale extract, orange extract, orange flower water, seaweed extract, persimmon tannin, pueraria root extract, Japanese valerian extract, cattail extract, Chamomile (matricaria) extract, oil soluble Chamomile (matricaria) extract, Chamomile (matricaria) distillate, Avena
15 sativa (oat) kernel extract, carrot extract, oil soluble carrot extract, carrot oil, Artemisia capillaris extract, Glycyrrhiza glabra (licorice) extract, powdered Glycyrrhiza glabra (licorice) extract, Glycyrrhiza glabra (licorice) extract flavonoid, cantharides tincture, raspberry extract, kiwi extract, cinchona
20 extract, cucumber extract, apricot kernel extract, quince seed extract, gardenia florida extract, Sasa albomarginata extract, Sophora root extract, walnut shell extract, Citrus paradisi (grapefruit) extract, Clematis vitalba leaf extract, black sugar extract, chlorella extract, mulberry bark extract, Cinnamon bark
25 extract, Gentian extract, Geranium herb extract, black tea extract, Nuphar extract, burdock root extract, oil soluble burdock root extract, wheat germ extract, hydrolyzed wheat powder, rice bran extract, fermented rice bran extract, Symphytum officinale (comfrey) extract, Asiasarum root extract, Crocus sativus (saffron)
30 extract, Saponaria officinalis extract, oil soluble salvia extract, Crataegus cuneata fruit extract, Zanthoxylum fruit extract,

Lentinus edodes extract, powdered Lentinus edodes extract,
Rehmannia root extract, Lithospermum root extract, oil soluble
Lithospermum root extract, Perilla herb extract, linden extract,
oil soluble Tilia europaea extract, Filipendula extract, Peony
5 root extract, Coix lacryma-jobi extract, ginger extract, oil
soluble ginger extract, ginger tincture, Acorus calamus root
extract, Betula pendula (birch) extract, oil soluble Betula alba
(birch) extract, Betula pendula (birch) sap, Lonicera japonica
extract, Equisetum arvense extract, oil soluble Equisetum arvense
10 extract, scordinin, stevia extract, ivy extract, Crataegus
oxyacantha (whitethorn) extract, sambucus extract, Juniperus
communis extract, Achillea millefolium extract, oil soluble Achillea
millefolium extract, Mentha piperita (peppermint) extract, Salvia
officinalis (sage) extract, oil soluble Salvia officinalis (sage)
15 extract, Salvia officinalis (sage) water, Malva Sylvestris (mallow)
extract, Apium graveolens (celery) extract, Cnidium officinale
extract, Cnidium officinale water, Swertia herb extract, Glycine
max (soybean) extract, Jujube extract, thyme extract, green tea
extract, tea leaf dry distilled solution, tea seed extract, clove
20 extract, Citrus unshiu peel extract, Camellia japonica extract,
Centella asiatica extract, oil soluble walnut extract, duku extract,
Terminalia sericea extract, Capsicum tincture, Japanese angelica
root extract, oil soluble Japanese angelica root extract, Japanese
angelica root water, Calendula officinalis flower extract, oil
25 soluble Calendula officinalis flower extract, soy milk powder,
peach seed extract, Bitter orange peel extract, Houttuynia cordata
extract, Solanum lycopersicum (tomato) extract, Potentilla
tormentilla Schrk (Rosaceae) extract, fermented soybeans extract,
Ginseng extract, oil soluble Ginseng extract, Allium sativum
30 (garlic) extract, wild rose extract, oil soluble wild rose extract,
malt extract, malt root extract, Ophiopogon tuber extract, parsley

extract, rye leaf juice concentrate, peppermint distillate, witch
hazel distillate, witch hazel extract, rose extract, parietaria
extract, Isodonis japonicus extract, Eriobotrya japonica leaf
extract, oil soluble Eriobotrya japonica leaf extract, coltsfoot
5 extract, hoelen extract, Ruscus aculeatus root extract, powdered
Ruscus aculeatus root extract, grape extract, grape leaf extract,
grape water, Hayflower extract, Luffa cylindrica fruit extract,
Luffa cylindrica fruit water, Carthamus tinctorius (safflower)
extract, oil soluble Tiliaplatyphyllos extract, lindendistillate,
10 Paeonia suffruticosa (peony) extract, Humulus lupulus (hops)
extract, oil soluble Humulus lupulus (hops) extract, pine extract,
Silybum marianum (milk thistle) extract, Aesculus hippocastanum
(horse chestnut) extract, oil soluble Aesculus hippocastanum (horse
chestnut) extract, Sapindus mukurossi extract, Melissa
15 officinalis (balm mint) extract, Melilotus officinalis (melilot)
extract, Prunus persica (peach) leaf extract, oil soluble Prunus
persica (peach) leaf extract, bean sprouts extract, Centaurea cyanus
flower extract, Centaurea cyanus flower distillate, Eucalyptus
globulus extract, Saxifrage extract, Lilium (lily) extract, Coix
20 seed extract, oil soluble Coix seed extract, Artemisia princeps
pampanini extract, Artemisia princeps pampanini water, Lavandula
angustifolia (lavender) extract, Lavandula angustifolia
(lavender) water, apple extract, Ganoderma lucidum extract, Lactuca
sativa (lettuce) extract, lemon extract, Astragalus sinicus
25 extract, Rosa centifolia (rose) flower water, Rosemarinus
officinalis (rosemary) extract, oil soluble Rosemarinus
officinalis (rosemary) extract, Anthemis nobilis extract and
Sanguisorba officinalis extract;

amino acids and peptides such as glycine, alanine, valine,
30 leucine, isoleucine, serine, threonine, phenylalanine, tyrosine,
tryptophan, cystine, cysteine, methionine, proline,

hydroxyproline, aspartic acid, asparagine, glutamic acid, glutamine, arginine, histidine, lysine, γ -aminobutyric acid, DL-pyrrolidonecarboxylic acid, ϵ -aminocaproic acid, hydrolyzed elastin, water soluble elastin, hydrolyzed collagen, water soluble collagen, casein, glutathione, wheat peptides and soybean peptide;

5 vitamins and factors acting like a vitamin such as: vitamin A and analogues thereof such as retinol, retinal, retinoic acid, retinol acetate and retinol palmitate; carotenoids such as α -carotene, β -carotene, γ -carotene, δ -carotene, lycopene, zeaxanthin, cryptoxanthin, echinenon and astaxanthin; vitamin B₁ and analogues thereof such as thiamines; vitamin B₂ and analogues thereof such as riboflavin; vitamin B₆ and analogues thereof such as pyridoxine, pyridoxal and pyridoxamine; vitamin B₁₂ and analogues thereof such as cyanocobalamin; folic acids, nicotinic acid, nicotinamide, pantothenic acids, biotins; vitamin C and analogues thereof such as L-ascorbic acid, sodium L-ascorbate, L-ascorbyl stearate, L-ascorbyl palmitate, L-ascorbyl dipalmitate, L-ascorbyl tetraisoalmitate, disodium L-ascorbate sulfate ester, magnesium L-ascorbyl, sodium L-ascorbyl phosphate, L-ascorbate-2-glucoside and magnesium L-ascorbate-2-phosphate; vitamin D and analogues thereof such as ergocalciferol and cholecalciferol; vitamin E and analogues thereof such as d- α -tocopherol, DL- α -tocopherol, dl- α -tocopherol acetate, dl- α -tocopherol succinate, β -tocopherol, γ -tocopherol and d- δ -tocopherol; ubiquinones, vitamin K and analogues thereof, carnitine, ferulic acid, γ -oryzanol, α -lipoic acid and orotic acid;

antiseptic agents such as benzoic acid, sodium benzoate, undecylenic acid, salicylic acid, sorbic acid, potassium sorbate, dehydroacetic acid, sodium dehydroacetate, isobutyl

30 paraoxybenzoate, isopropyl paraoxybenzoate, ethyl paraoxybenzoate, butyl paraoxybenzoate, propyl paraoxybenzoate,

benzyl paraoxybenzoate, methyl paraoxybenzoate, sodium paraoxybenzoate methyl, phenoxyethanol, light sensitive dye No. 101, light sensitive dye No. 201 and light sensitive dye No. 401;

antioxidizing agents such as butylhydroxyanisole, butylhydroxytoluene, propyl gallate, erythorbic acid, sodium erythorbate, para-hydroxyanisole and octyl gallate;

chelating agents to bind to a metal ion such as trisodium ethylenediamine hydroxyethyl triacetate, edetic acid, disodium edetate, trisodium edetate, tetrasodium edetate, sodium citrate, gluconic acid, phytic acid, sodium polyphosphate and sodium metaphosphate;

moisturizing agents such as hyaluronic acid, sodium hyaluronate, sodium chondroitin sulfate, sodium lactate, sodium pyrrolidone carboxylate, betaine, lactic acid bacteria fermented solution, yeast extract and ceramide;

anti-inflammatory agents such as glycyrrhizic acid, trisodium glycyrrhizinate, dipotassium glycyrrhizinate, monoammonium glycyrrhizinate, β -glycyrrhetinic acid, glycerin glycyrrhetinate, stearyl glycyrrhetinate, lysozyme chloride, hydrocortisone and allantoin;

pH adjusting agents such as sodium hydroxide, potassium hydroxide and triethanolamine;

salts such as sodium chloride, potassium chloride, magnesium chloride and sodium sulfate;

α -hydroxy acids such as citric acid, glycolic acid, tartaric acid and lactic acid;

whitening agents such as arbutin, α -arbutin and placenta extract;

essential oils such as *Archangelica officinalis* (angelica) oil, *Canangium odoratum* (ylang ylang) oil, *Canarium luzonicum* (elemi) oil, orange oil, *Chamomilla recutita* (matricaria) oil,

5 Anthemis nobilis oil, Elettaria cardamom (cardamon) oil, Acorus
calamus (calamus) oil, Ferula galbaniflua (galbanum) oil,
Cinnamomum camphora (camphor) oil, Daucus carota (carrot) seed
oil, Salvia sclarea (clary sage) oil, Citrus paradisi (grapefruit)
10 oil, Eugenia caryophyllus (clove) oil, Cinnamon bark oil,
Coriandrum sativum (coriander) oil, Cupressus sempervirens
(cypress) oil, Santalum album (sandalwood) oil, Juniperus
virginiana (cedarwood) oil, Cymbopogon nardus (citronella) oil,
Cinnamomum zeylanicum (Cinnamon) leaf oil, Jasmine officinale
15 (jasmine) absolute oil, Juniperus communis (juniper Berry) oil,
Zingiber officinale (ginger) extract, Mentha spicata (spearmint)
oil, Salvia officinalis (sage) oil, cedar oil, Pelargonium
graveolens (geranium) oil, Thymus vulgaris (thyme) oil, Melaleuca
alternifolia (tea tree) oil, Myristica fragrans (nutmeg) oil,
20 Melaleuca viridiflora (niaouli) oil, Citrus aurantium (neroli)
oil, pine oil, Ocimum basilicum (basil) oil, Mentha arvensis oil,
Pogostemon patchouli (patchouli) oil, Cymbopogon martini
(palmarosa) oil, Foeniculum vulgare (fennel) oil, Citrus bigaradia
(petitgrain) oil, Piper nigrum (black pepper) oil, Boswellia
25 carterii (frankincense) oil, Vetiveria zizanioides (vetiver) oil,
Mentha piperita (peppermint) oil, Citrus bergamia (bergamot) oil,
benzoin oil, Aniba rosaeodora (bois de rose) oil, Origanum majorana
(marjoram) oil, mandarin oil, Conium maculatum (myrrh) oil,
Melissa officinalis (balm mint) oil, Eucalyptus globulus oil,
30 Citrus junos oil, Citrus aurantifolia (lime) oil, Ravensara
aromaticum (ravensara) oil, Lavandula latifolia (lavandin) oil,
Lavandula angustifolia (lavender) oil, Tilia vulgaris (linden)
oil, lemon oil, lemon grass oil, rose oil, Aniba rosaeodora
(rosewood) oil, Rosemarinus officinalis (rosemary) oil and
30 Levisticum officinale (lovage) oil;

terpenes such as limonene, pinene, terpinene, terpinolene,

myrcene and longifeelene;

fragrance, water, and the like.

Furthermore, to the external preparation for skin of the invention may also be added any existing raw material of cosmetics at a general concentration. All raw materials of cosmetics described in, for example, Keshouhin genryou kizyun (Standards of raw materials of cosmetics), second edition, notes, edited by Society of Japanese Pharmacopoeia, 1984 (YAKUJI NIPPO LIMITED.), Keshouhin genryou kizyun-gai seibun kikaku (Standards of raw materials of cosmetics, nonstandard ingredients), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin genryou kizyun-gai seibun kikaku tsuiho (Standards of raw materials of cosmetics, nonstandard ingredient, Supplement), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin syubetsu kyoka kizyun (Standards of cosmetic classification permission), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1993 (YAKUJI NIPPO LIMITED.), Keshouhin syubetsu haigou seibun kikaku (Standards of cosmetic classification ingredients), under the editorship of Pharmaceutical Affairs Bureau Evaluation and Registration Division, 1997 (YAKUJI NIPPO LIMITED.), Keshouhin genryou jiten (Dictionary of raw materials of cosmetics), 1991 (Nikko Chemicals Co., Ltd.), Atarashii Keshouhinkinou Sozai 300 (New 300 raw materials having cosmetic functions), 2002 (CMC Publishing Co., Ltd) and the like may be used.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereunder, the present invention will be specifically explained with reference to the Examples, however, the present

invention is not limited to these Examples.

Example 1:

Under nitrogen atmosphere, into a sufficiently dried Schlenk
5 tube, 13.0 g of 1,6-anhydro- β -D-glucopyranose (manufactured by
Tokyo Kasei Kogyo Co., Ltd.), 12.5 ml of dry propylene
carbonate (manufactured by Sigma-Aldrich Co.) and 66 mass % of
2-butylnyltetramethylene sulfonium hexafluoroantimonate (65.8
10 μ l) (manufactured by ASAHI DENKA CO., LTD.) were charged. Then,
the Schlenk tube was placed in an oil bath, and the oil bath was
heated to 100 °C so as to thoroughly dissolve
1,6-anhydro- β -glucopyranose. Subsequently, the oil bath was
further heated to 130 °C while stirring, so as to allow polymerization
to begin. After 30 minutes' reaction, the polymerization solution
15 was added into methanol to stop the polymerization reaction. After
removing the solvent, reprecipitation was repeated with water and
methanol. The resultant solution was further dialyzed for
purification and freeze-dried to obtain 5.3 g of multi-branched
polysaccharide A in white powder. The yield was 41 %. The
20 multi-branched polysaccharide A was subjected to ^1H -NMR and ^{13}C -NMR
analyses to confirm the structure. Moreover, the weight average
molecular weight of the multi-branched polysaccharide A was 20,000
(light scattering method), and the branching degree was 0.38.

25 Example 2:

Skin lotions as shown in Table 1 were prepared by a conventional
method. Ten females of age 20-30 used these lotions and their
feedbacks immediately after applying each lotion and after spending
one hour with the lotion applied onto the skin at a humidity of
30 20 % were shown in Table 2. The results revealed that by using
Sample 1-1 containing multi-branched polysaccharide A obtained

in Example 1, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

5

Table 1

| Sample | 1-1 | 1-2 | 1-3 |
|---------------------------------|---------|---------|---------|
| Multi-branched polysaccharide A | 0.50% | — | — |
| Glycogen | — | 0.50% | — |
| 1,3-buthylene glycol | 5.00% | 5.00% | 5.00% |
| Ethylalcohol | 5.00% | 5.00% | 5.00% |
| Citric acid | 0.01% | 0.01% | 0.01% |
| Sodium citrate | 1.00% | 1.00% | 1.00% |
| Methyl paraben | 0.20% | 0.20% | 0.20% |
| Pure water | 88.29% | 88.29% | 88.79% |
| | 100.00% | 100.00% | 100.00% |

Table 2

| Sample | 1-1 | 1-2 | 1-3 |
|---|-----|-----|-----|
| Moisture feeling immediately after applying | 9 | 8 | 2 |
| Moisture feeling after the skin dried | 8 | 4 | 0 |
| Taut feeling immediately after applying | 0 | 0 | 0 |
| Taut feeling after the skin dried | 1 | 6 | 9 |

Example 3:

10 With respect to three females of age 30-40, the skin lotions shown in Table 1 were applied onto the skin of the flexor aspect of the forearm twice a day, one time in the morning and the other in the evening, for seven days. The moisture levels in the keratin layer were measured and compared on the morning of the eighth day
 15 with a conductivity value determined through high-frequency inductance method by using an impedance meter (SKICON-200:manufactured by IBS Co., Ltd.) as an index, and the results were shown in Table 3. According to the results, by using

sample 1-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

5

Table 3

| | Before | After 1-1 applied | After 1-2 applied | After 1-3 applied |
|--------------|--------|----------------------|----------------------|----------------------|
| Conductivity | 100 | 183 | 175 | 118 |

Example 4:

Skin lotions as shown in Table 4 were prepared by a conventional method and applied in the same manner as in Example 3. The moisture levels in the keratin layer were measured and compared on the morning of the eighth day by using as an index a conductivity value determined through high-frequency inductance method by an impedance meter, and the results were shown in Table 5. According to the results, by using sample 2-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

Table 4

| Sample | 2-1 | 2-2 | 2-3 |
|---------------------------------|--------|--------|--------|
| Multi-branched polysaccharide A | 0.5% | — | — |
| Glycine | — | 0.5% | — |
| 1,3-butylene glycol | 9.5% | 9.5% | 9.5% |
| Ethyl alcohol | 39.6% | 39.6% | 39.6% |
| Castor oil | 4.9% | 4.9% | 4.9% |
| Methylparaben | 0.2% | 0.2% | 0.2% |
| Pure Water | 45.3% | 45.3% | 45.8% |
| | 100.0% | 100.0% | 100.0% |

Table 5

| | Before | After 2-1 applied | After 2-2 applied | After 2-3 applied |
|--------------|--------|----------------------|----------------------|----------------------|
| Conductivity | 100 | 189 | 145 | 125 |

Example 5:

Milky lotions as shown in Table 6 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion applied onto the skin at a humidity of 20 % were shown in Table 7. The results revealed that by using Sample 3-1 containing multi-branched polysaccharide A obtained in Example 1, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

Table 6

| Sample | 3-1 | 3-2 | 3-3 |
|---------------------------------|--------|--------|--------|
| Multi-branched polysaccharide A | 1.0% | — | — |
| Hdroxyethylcellulose | — | 0.5% | — |
| Xanthan gum | — | 0.5% | — |
| Glycerin | 8.0% | 8.0% | 8.0% |
| 1,3-buthylene glycol | 2.0% | 2.0% | 2.0% |
| Sodium citrate | 1.0% | 1.0% | 1.0% |
| Polyethylene glycol 50 | 0.5% | 0.5% | 0.5% |
| Methyl paraben | 0.2% | 0.2% | 0.2% |
| Pure Water | 87.3% | 87.3% | 88.3% |
| | 100.0% | 100.0% | 100.0% |

Table 7

| Sample | 3-1 | 3-2 | 3-3 |
|---|-----|-----|-----|
| Moisture feeling immediately after applying | 9 | 8 | 5 |
| Moisture feeling after the skin dried | 7 | 5 | 0 |
| Taut feeling immediately after applying | 0 | 0 | 1 |
| Taut feeling after the skin dried | 1 | 7 | 6 |

Example 6:

Milky lotions as shown in Table 6 were applied in the same manner as in Example 3. The moisture levels in the keratin layer measured on the morning of the eighth day using as an index a conductivity value determined through high-frequency inductance method by an impedance meter, and the results were shown in Table 8. According to the results, by using sample 3-1 containing multi-branched polysaccharide A obtained in Example 1, enhancement in conductivity was observed, which indicated that the moisture in the keratin layer was increased to replenish the skin moisture.

Table 8

| | Before | After 3-1 applied | After 3-2 applied | After 3-3 applied |
|--------------|--------|----------------------|----------------------|----------------------|
| Conductivity | 100 | 192 | 178 | 125 |

Example 7:

Under nitrogen atmosphere, into a sufficiently dried flask, 1.0 g of multi-branched polysaccharide A and dry pyridine were charged. Then, 11.5 g of leucine ethylester isocyanate was slowly added dropwise and the mixture was allowed to react at 100 °C for 24 hours. After the reaction, the reaction solution was poured into methanol. After the solvent was distilled off, and reprecipitation was repeated with water and methanol. The resultant solution was further dialyzed for purification and freeze-dried to obtain 1.96 g of multi-branched polysaccharide derivative B in white powder. According to the elemental analysis,

the substitution degree of the compound was 2.9.

Example 8:

Milky lotions as shown in Table 9 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion being applied onto the skin at a humidity of 20 % were shown in Table 10. The results revealed that by using Sample 4-1 containing multi-branched polysaccharide derivative B obtained in Example 7, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

Table 9

| Sample | 4-1 | 4-2 | 4-3 |
|--|--------|--------|--------|
| Multi-branched polysaccharide derivative B | 1.0% | — | — |
| Hydroxyethylcellulose | — | 0.5% | — |
| Xanthan gum | — | 0.5% | — |
| Glycerin | 8.0% | 8.0% | 8.0% |
| 1,3-buthylene glycol | 2.0% | 2.0% | 2.0% |
| Sodium citrate | 1.0% | 1.0% | 1.0% |
| Polyethylene glycol-50 | 0.5% | 0.5% | 0.5% |
| Methylparaben | 0.2% | 0.2% | 0.2% |
| Pure water | 87.3% | 87.3% | 88.3% |
| | 100.0% | 100.0% | 100.0% |

Table 10

| Sample | 4-1 | 4-2 | 4-3 |
|---|-----|-----|-----|
| Moisture feeling immediately after applying | 9 | 8 | 5 |
| Moisture feeling after the skin dried | 6 | 5 | 0 |
| Taut feeling immediately after applying | 0 | 0 | 1 |
| Taut feeling after the skin dried | 1 | 7 | 6 |

Example 9:

Under nitrogen atmosphere, into a sufficiently dried Schlenk tube, 1.7 g of 1,6-anhydro- β -D-mannopyranose and 3.5 ml of dry propylene carbonate were charged. Then, the Schlenk tube was placed in an oil bath, and the oil bath was heated to 90 °C so as to thoroughly dissolve 1,6-anhydro- β -D-mannopyranose. Subsequently, 66 % by mass (11.4 μ l) of 3-methyl-2-butynyltetramethylenesulfonium hexafluoroantimonate was added to allow polymerization to begin. After 20 minutes' reaction, the polymerization solution was poured into methanol to stop the polymerization reaction. After removing the solvent, reprecipitation was repeated with water and acetone. The resultant solution was further dialyzed for purification and freeze-dried to obtain 1.11 g of multi-branched polysaccharide C in white powder. The yield was 64 %. The multi-branched polysaccharide C was subjected to $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analyses to confirm the structure. Moreover, the weight average molecular weight of the multi-branched polysaccharide C was 80,000 (light scattering method), and the branching degree was 0.43.

Example 10:

Milky lotions as shown in Table 11 were prepared by a conventional method. Ten females of age 20-30 used these lotions and their feedbacks immediately after applying each lotion and after spending one hour with the lotion being applied onto the skin at a humidity of 20 % were shown in Table 12. The results revealed that by using Sample 5-1 containing multi-branched polysaccharide C obtained in Example 9, the moisture feeling of the skin was preserved from immediately after applying the lotion to the time when the skin became dry, and even after the skin became dry, no taut feeling of the skin occurred.

Table 11

| Sample | 5-1 | 5-2 | 5-3 |
|--|--------|--------|--------|
| Multi-branched polysaccharide derivative C | 0.50% | — | — |
| Glycogen | — | 0.50% | — |
| 1,3-buthylene glycol | 5.00% | 5.00% | 5.00% |
| Ethyl alcohol | 5.00% | 5.00% | 5.00% |
| Citric acid | 0.01% | 0.01% | 0.01% |
| Sodium citrate | 1.00% | 1.00% | 1.00% |
| Methylparaben | 0.20% | 0.20% | 0.20% |
| Pure Water | 88.29% | 88.29% | 88.79% |
| | 100.0% | 100.0% | 100.0% |

Table 12

| Sample | 5-1 | 5-2 | 5-3 |
|---|-----|-----|-----|
| Moisture feeling immediately after applying | 10 | 8 | 2 |
| Moisture feeling after the skin dried | 8 | 4 | 0 |
| Taut feeling immediately after applying | 0 | 0 | 0 |
| Taut feeling after the skin dried | 0 | 6 | 9 |

5 INDUSTRIAL APPLICABILITY

As described above, according to the present invention where a small amount of multi-branched polysaccharide and/or derivatives thereof is blended in an external preparation for the skin, an excellent external preparation for the skin having effects of giving sufficient moisturized feeling and not causing uncomfortable taut feeling to the skin can be provided.